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# Time-reversal symmetry breaking in superconductors through loop supercurrent order

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We propose a novel superconducting ground state where microscopic supercurrent loops form spontaneously within a unit cell at the superconducting transition temperature with only uniform, onsite and intra-orbital singlet pairing. As a result of the circulating currents time-reversal symmetry is spontaneously broken in the superconducting state. Using Ginzburg-Landau theory we describe in detail how these currents emerge in a toy model. We discuss the crystallographic symmetry requirements more generally to realize such a state and show that they are met by the  $\text{Re}_6\text{X}$  ( $\text{X} = \text{Zr}, \text{Hf}, \text{Ti}$ ) family of time-reversal symmetry-breaking, but otherwise seemingly conventional, superconductors. We estimate an upper bound for the resulting internal magnetic fields and find it to be consistent with recent muon-spin relaxation experiments.

## I. INTRODUCTION

Many unconventional superconductors not only break global  $U(1)$  gauge symmetry but also other symmetries, such as time-reversal symmetry (TRS). TRS breaking has been observed in quite a few superconductors [1] mainly using muon-spin rotation and relaxation ( $\mu\text{SR}$ ) experiments, e.g.  $(\text{U}, \text{Th})\text{Be}_{13}$  [2],  $\text{Sr}_2\text{RuO}_4$  [3],  $\text{UPt}_3$  [4],  $(\text{Pr}, \text{La})(\text{Ru}, \text{Os})_4\text{Sb}_{12}$  [5, 6],  $\text{PrPt}_4\text{Ge}_{12}$  [7],  $\text{LaNiC}_2$  [8],  $\text{LaNiGa}_2$  [9],  $\text{SrPtAs}$  [10],  $\text{Re}$  [11],  $\text{Re}_6(\text{Zr}, \text{Hf}, \text{Ti})$  [12–14],  $\text{Zr}_3\text{Ir}$  [15],  $\text{LaPt}_3\text{P}$  [16],  $\text{Lu}_5\text{Rh}_6\text{Sn}_{18}$  [17] and  $\text{La}_7(\text{Ir}, \text{Rh})_3$  [18, 19]. Other direct observations of TRS breaking exist only in a handful of systems, namely optical Kerr effect in  $\text{Sr}_2\text{RuO}_4$  [20] and  $\text{UPt}_3$  [21], and bulk magnetization in  $\text{LaNiC}_2$  [22].

Unfortunately the fundamental question of the pairing symmetry in most of these superconductors with broken TRS remains unsettled. Most pairing scenarios [23–25] involve inter-site or inter-orbital pairing resulting in symmetry-required nodes in the quasiparticle spectrum. These are, however, strongly contested and can not explain recent observations of broken TRS in fully-gapped superconductors [1]. In the cases of  $\text{LaNiGa}_2$  and  $\text{LaNiC}_2$  [26, 27] thermodynamic measurements imply a two-gap spectrum, leading to the proposal of a non-unitary triplet state with inter-orbital pairing [28, 29]. Even this pairing state, however, cannot explain TRS breaking, for example in  $\text{Re}_6(\text{Hf}, \text{Ti}, \text{Zr})$  [12–14, 30–33] and  $\text{La}_7(\text{Ir}, \text{Rh})_3$  [18, 19, 25] families of superconductors which show otherwise conventional Bardeen–Cooper–Schrieffer (BCS) behaviour. This leaves us asking the following, seemingly-heretical question: can a weak-coupling BCS-type superconducting state with uniform, onsite, intra-orbital and singlet pairing spontaneously break TRS?

Here we address the above question on very general symmetry grounds within the standard Ginzburg-Landau approach [34–36]. Surprisingly, we find that the answer can be affirmative: TRS can be broken at the superconducting transition temperature  $T_c$  through the spontaneous formation of loop supercurrents linking symmetry-related sites or orbitals within the same unit cell (Figs. 1(e) and (f)). In this loop supercurrent state, *the microscopic supercurrent loops form a static order giving rise to an induced magnetic field detectable by experiments such as  $\mu\text{SR}$* . The essential ingredients for stabilizing such a state are: 1) more than two distinct symmetry-related sites within the unit cell, 2) intrinsically degenerate superconducting instability channel arising from multi-dimensional real or pseudoreal irreducible representations of the point group, and 3) symmetry-allowed degenerate superconducting instability channel with nontrivial phases between the components. Using a simple toy crystal structure we show that the normal-state susceptibility can diverge in a degenerate channel with left- and right-circulating supercurrents, with a state featuring net loop supercurrents stabilising below  $T_c$ . We extend our analysis to the more complex crystal structure of the  $\text{Re}_6(\text{Hf}, \text{Ti}, \text{Zr})$  family of unconventional superconductors, as a concrete example and find similar physics. We discuss the conditions for this exotic state to be the dominant instability and argue that it is compatible with a fully-gapped excitation spectrum.

We note that the proposed loop supercurrent state is qualitatively different from the frustration induced  $s+i s$  state usually proposed for some of the Iron-based superconductors [37–44]. The  $s+i s$  state is realized in multiband superconductors with an odd number of bands (more than two) as a result of frustration in the phases of the order parameters in different bands caused by strong interband repulsive interactions [37, 38, 41]. This state does not break any additional crystalline symmetries other than the usual  $U(1)$  symmetry and by itself does not produce spontaneous currents detectable in  $\mu\text{SR}$  for example. It requires breaking additional crystalline symmetries externally for producing discernible spontaneous currents [42]. The loop supercurrent state on the other hand is a weak-coupling

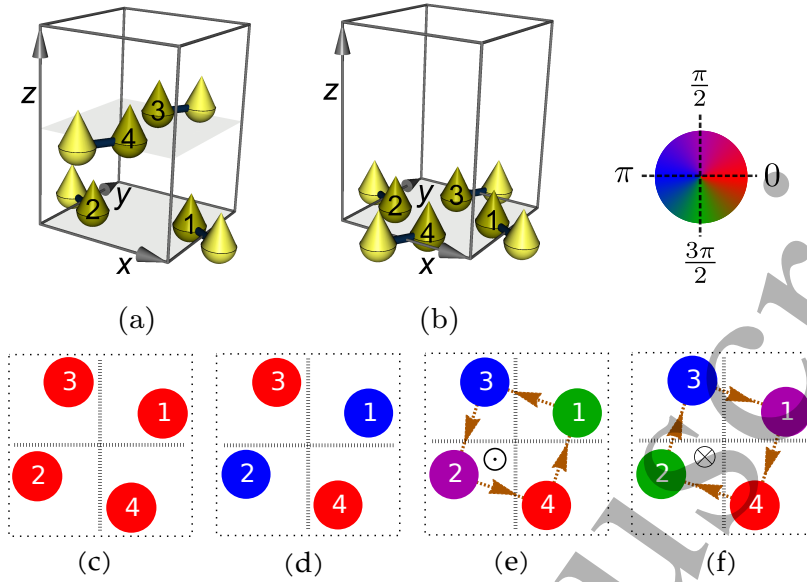


FIG. 1. Tetragonal unit cell (lattice parameters  $a, a, c$ ) and possible superconducting instabilities for a toy model. Crystal fields along the  $z$ -axis break inversion symmetry. (c) – (f): top view of the four symmetry-allowed superconducting instabilities for both models with uniform, onsite singlet pairing. The color wheel depicts the phase of the superconducting order parameter. The TRS-breaking instability is a linear combination of (e) and (f), which are degenerate. The arrows show the direction of the circulating supercurrents within a unit cell in each case.

instability stabilized in systems with onsite singlet pairing. It breaks additional crystalline symmetries other than the  $U(1)$  symmetry and is a chiral state which induces a spontaneous magnetic field detectable by  $\mu\text{SR}$ .

## II. TOY MODEL

To illustrate the idea, we construct a simple model with low symmetry but multiple symmetry-related sites within a unit cell. Two unit cells with noncentrosymmetric primitive tetragonal structure, one of them with a nonsymmorphic space group ( $P4_2$ ), the other symmorphic ( $P4$ ), are schematically shown in Figs. 1 (a) and (b) respectively. The factor group  $P4_2/\mathcal{T}$  (where  $\mathcal{T}$  is the group of pure translations) is an Abelian group of “point-like” symmetries (symmetry elements: Identity ( $E$ ), rotation by  $\pi$  about the  $z$ -axis ( $C_2^z$ ), left-handed screw  $S_L = T_{(0,0,1/2)}C_{4+}^z$  and right-handed screw  $S_R = T_{(0,0,1/2)}C_{4-}^z$  with  $T_{(n_1,n_2,n_3)}$  being the translation operator) isomorphic to the corresponding point group of the Bravais lattice  $C_4$  (the cyclic group of order 4) which is also the point group of  $P4$ . So, the group of “point-like” symmetries for both model systems has only 1D irreducible representations, however as is well known, two of these become degenerate due to the presence of TRS in the normal state, making an instability to a superconducting state with broken TRS possible [45].

We consider the simplest case of onsite singlet pairing which is uniform between unit cells but can have distinct values at different sites within a unit cell. We define

$$|\Delta\rangle = (\Delta_1, \Delta_2, \Delta_3, \Delta_4) \quad (1)$$

where  $\Delta_i$  is the pairing potential at the  $i$ -th site within a unit cell. The Ginzburg-Landau free energy of the system can be written as

$$\mathcal{F} = \langle \Delta | \hat{\alpha} | \Delta \rangle + (\langle \Delta | \otimes \langle \Delta |) \hat{\beta} (| \Delta \rangle \otimes | \Delta \rangle) + \dots \quad (2)$$

where  $\hat{\alpha}$  is the inverse pairing susceptibility (IPS) matrix and  $\hat{\beta}$  is a fourth order tensor. As usual,  $\hat{\alpha}$  and  $\hat{\beta}$  are constrained [46] by the requirements that  $\mathcal{F}$  is real and invariant under the normal-state symmetry group  $G = G_0 \otimes U(1) \otimes \mathcal{T}$ , where  $G_0$  is the group of “point-like” symmetries of the crystal and spin rotation symmetries, and  $\mathcal{T}$  is the group of TRS [34–36].

We first focus on the 2nd-order term of the free energy in Eq. (2) to determine all the possible symmetry-allowed superconducting instabilities. The  $\hat{\alpha}$  matrix in our model can be parametrized by only three real numbers  $p_i$  ( $i = 1,$

2 and 3):

$$\hat{\alpha} = \begin{bmatrix} p_1 & p_2 & p_3 & p_3 \\ p_2 & p_1 & p_3 & p_3 \\ p_3 & p_3 & p_1 & p_2 \\ p_3 & p_3 & p_2 & p_1 \end{bmatrix}. \quad (3)$$

It has three eigenvalues, corresponding to three distinct superconducting instabilities: two non-degenerate eigenvalues  $\lambda_{1,2} = \mp 2p_3 + p_2 + p_1$  with pairing potentials  $|\Delta\rangle = (1, 1, 1, 1)$  and  $(1, -1, 1, -1)$ , respectively, and one doubly-degenerate eigenvalue  $\lambda_3 = p_1 - p_2$  with  $|\Delta\rangle$  a linear combination of  $(-i, i, -1, 1)$  and  $(i, -i, -1, 1)$ . The phase structures of  $|\Delta\rangle$  are shown graphically in Figs. 1(c) – (f). Fig. 1(c) corresponds to a conventional s-wave type instability whereas the one in Fig. 1(d) is an instability with cyclic sign change in the onsite order parameter. Interestingly, the other two instabilities (shown in the Figs. 1(e) and (f)) have order parameters with non-trivial phases at different sites.

Generally speaking, the presence of  $D > 1$  irreducible representations of  $G$  implies the possibility of degenerate superconducting instabilities and is a necessary condition for a superconducting ground state with broken TRS [34–36]. This type of instability usually involves inter-site pairing (such as  $p$ -wave,  $d$ -wave etc.) whose phase changes as a function of the direction of the bond along which the pairing takes place. Such pairing states are, however, not compatible with the onsite pairing assumed in Eq. (1). The requirement for  $D > 1$  irreducible representations is thus replaced with a more restrictive one, namely for the  $\hat{\alpha}$  matrix to have at least one degenerate eigenvalue. This in turn requires, in addition to a  $D > 1$  irreducible representation, a sufficient number of distinct, but symmetry-related sites within the unit cell. As a point of comparison, with onsite pairing and one site per unit cell we only obtain BCS-type superconductivity. Similarly, in a model with two sites per unit cell, such as the one discussed by Fu and Berg [47] in the context of doped topological insulators, the only onsite, intra-orbital, singlet-pairing instabilities are: 1) conventional one with the same pairing potential on both sites  $(1, 1)$  and 2) one with the pairing potentials on the two sites having opposite signs  $(1, -1)$ . TRS-breaking instabilities in this case require inter-site pairing [47]. Finally, we note that the nonsymmorphic toy crystal structure (shown in Fig. 1(a)) can be continuously tuned to the symmorphic one (shown in Fig. 1(b)) by changing the position of the plane at  $(0, 0, c/2)$  containing the sites 3 and 4 along the  $z$ -axis via intermediate structures with lower symmetry. In that case, the sites 1 and 2 are not symmetry-related to the sites 3 and 4, and the states with broken TRS discussed here are also not allowed.

The doubly degenerate instability occurs at  $T_c$  if  $\lambda_3 = 0$  first rather than  $\lambda_1$  or  $\lambda_2$ , leading to

$$p_2 > |p_3|. \quad (4)$$

We note that the above condition refers to the relative size and signs of two of the off-diagonal terms in the  $\hat{\alpha}$  matrix, not to how they compare to the diagonal terms. Whether Eq. (4) is obeyed depends on details of the model and is not dictated by symmetry. If it is, we can write  $\lambda_3 = (T - T_c)\dot{\alpha}$  where we assume  $\dot{\alpha} > 0$ . As usual we then have to check whether the quartic terms in the free energy stabilise a TRS-breaking state- which in our case takes the form of a phase difference between different sites of the unit cell. In that case, we can think of any two sites as a microscopic Josephson junction of two superconductors with a phase difference between them. A Josephson current can then flow between the two sites. For the superconducting instability in Fig. 1(e) (Fig. 1(f)) the Josephson current flows in a loop within the unit cell in the anticlockwise (clockwise) direction. We thus define these two states to be left-circulating ( $|L\rangle$ ) and right-circulating ( $|R\rangle$ ) loop supercurrent states, respectively.

Let us now investigate the fate of the doubly-degenerate instability by analyzing the effect of the quartic order term in Eq. (2). As with  $\hat{\alpha}$ , we use general symmetry properties to constrain the  $\hat{\beta}$  tensor (see Appendix A). To this end, we write

$$|\Delta\rangle = \eta_L |L\rangle + \eta_R |R\rangle \quad (5)$$

where  $\eta_L = |\eta_L|e^{i\varphi_L}$  and  $\eta_R = |\eta_R|e^{i\varphi_R}$  are complex coefficients. The system now has a new two-component order parameter  $\eta = (\eta_L, \eta_R)$  and the free energy needs to satisfy the condition:  $\mathcal{F}(\eta_L, \eta_R) = \mathcal{F}(\eta_L^*, \eta_R^*)$ . Using the parametrization:  $|\eta_L| = |\eta| \cos(\gamma)$  and  $|\eta_R| = |\eta| \sin(\gamma)$ , and defining  $\theta \equiv (\varphi_L - \varphi_R)$ , the free energy up to quartic order can be written as

$$\mathcal{F}(\theta, \gamma) = a_{eff} |\eta|^2 + b_{eff}(\theta, \gamma) |\eta|^4. \quad (6)$$

Here  $a_{eff} = (T - T_c)\dot{\alpha}$  and,  $b_{eff}(\theta, \gamma)$ , a function of  $\theta$  and  $\gamma$ , depends on four numbers  $\beta_i$  ( $i = 1, \dots, 4$ ) that parametrize  $\hat{\beta}$  in the subspace defined by Eq. (5) (the general form of  $\hat{\beta}$  and explicit formula for  $b_{eff}(\theta, \gamma)$  are given in Appendix A). The TRS-related pair of states are now described by  $(\theta, \gamma)$  and  $(\theta, \pi/2 - \gamma)$ . Below  $T_c$ , the free energy is stable for  $b_{eff} > 0$  and has minima when  $b_{eff}(\theta, \gamma)$  is minimum for fixed  $\beta_i$ -parameters. The minima of the free



energy always come in degenerate pairs. These two degenerate states are related by TRS and have loop supercurrents of the same strength but in opposite directions. The direction and strength of this circulating current depend on the phases of the different components of  $|\Delta\rangle$  at a given  $(\theta, \gamma)$ . In particular, there is left-circulating current for  $0 < \gamma < \pi/4$  and right-circulating current for  $\pi/4 < \gamma < \pi/2$ .

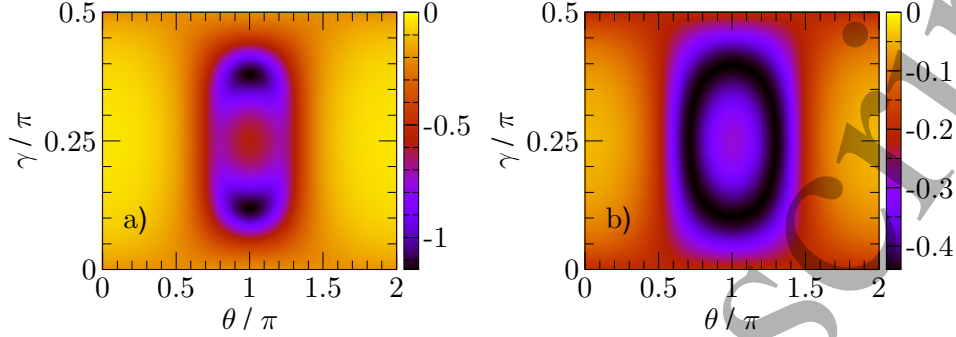


FIG. 2. Ginzburg-Landau free energy up to quartic order for our toy model below  $T_c$  with  $a_{eff}/T_c = -0.9$  and  $\beta_2/\beta_1 = 1.5$ . a) Two generic TRS-related degenerate free-energy minima for  $\beta_3/\beta_1 = 1.2$  and  $\beta_4/\beta_1 = 2.0$ . The minima at  $(\theta = \pi, \gamma = 0.12\pi)$  and  $(\theta = \pi, \gamma = 0.38\pi)$  correspond to left-circulating and right-circulating loop supercurrent states respectively with current  $I_c$ . b) A ring of degenerate free energy minima for  $\beta_4 = \beta_2$  and  $\beta_3/\beta_1 = 0.9$ .

The Ginzburg-Landau free energy for two particular choices of the  $\beta_i$ -parameters is plotted in Fig. 2. Fig. 2(a) shows the generic case, when the free energy has only a pair of degenerate TRS-related minima with finite loop supercurrents. In the superconducting state, the system spontaneously chooses one of these degenerate ground states, thus breaking TRS. As shown in the figure, the valley of stability surrounding each of these degenerate minima is strikingly anisotropic. This anisotropy changes as the Ginzburg-Landau parameters are varied until, for  $\beta_4 = \beta_2$  and  $(\beta_3/\beta_1)^2 < \beta_2/\beta_1$ , there are no longer two separate minima but a continuous ring of degenerate ground states satisfying  $\sin(2\gamma)\cos(\theta) = -\beta_3/\beta_2$ . An example of this is shown in Fig. 2(b). In this regime, the superconducting state spontaneously breaks an emergent continuous symmetry involving intertwined phase and amplitude degrees of freedom of the TRS-breaking order parameter. The low-lying collective excitations in this case are expected to be an exotic type of Goldstone boson whose study lies outside the remit of this article. Note that the pairing potential describing the loop supercurrent ground state varies within a unit cell resulting in breaking of some of the crystalline symmetries (e.g. for the toy model these are symmetries featuring the  $C_4$ -rotation). The order parameter for the continuous phase transition to the loop supercurrent state, however, is the overall pairing amplitude which increases from zero continuously as a function of decreasing the temperature below  $T_c$  and is uniform throughout the sample.

The loop supercurrent ground state can be realized in a candidate material if all of the following three conditions are satisfied. 1) The material needs to have more than two distinct but symmetry-related sites within a unit cell because at least three sites are necessary for the formation of a microscopic supercurrent loop. 2) The point group corresponding to the space group symmetry of the crystal must have at least one degenerate (multi-dimensional) real or pseudoreal (as in the case of the  $C_4$  point group discussed earlier) irreducible representations. 3) The quartic order term in the Ginzburg-Landau free energy needs to be constructed and from the stability diagram it has to be confirmed that indeed a multicomponent order parameter with nontrivial phase difference between its components is allowed in some region in the space of Ginzburg-Landau parameters.

Usually in discussing superconducting states with unconventional pairing, the pairing potential is constructed from  $\mathbf{k}$ -dependent basis functions of the relevant irreducible representation [34–36]. Such functions often vanish at high-symmetry directions in the  $\mathbf{k}$ -space leading to symmetry-required nodes in the quasi-particle spectrum. In contrast, our basis is made up of  $\mathbf{k}$ -independent vectors of the form shown in the Eq. (1). This translates into a  $\mathbf{k}$ -dependent gap function on the Fermi surface through form factors emerging from the band structure. Since the four components of the gap function do not all have the same phase, this can lead to nodes, however they are not located in high-symmetry directions in general. In other words, although the structure of the loop supercurrent state is constrained by symmetry in the usual way, the locations of any zeroes in the quasi-particle spectrum are accidental. This allows for the spectrum to be fully gapped even when the Fermi surfaces cut the high-symmetry axes in the Brillouin zone. For a given crystal structure, the quasi-particle spectrum will depend on details of the band structure such as the relative strength of individual hopping terms. Its calculation requires a more microscopic model than those used here and is beyond the scope of this article.

Note that the spontaneous TRS breaking by the loop supercurrent state is qualitatively different from the fluctuating single-electron loop-currents proposed to explain possible TRS breaking in the pseudogap phase of the cuprate

superconductors [48, 49]. In our case the spontaneous TRS breaking occurs in the superconducting state due to spontaneous formation of a *static order of microscopic Josephson current loops*, involving Cooper pairs. Any such currents present above  $T_c$  would have to result from superconducting fluctuations rather than from a competing order parameter, as in the Refs. [48, 49]. A discussion of loop currents in a chiral superconducting state can be found in Ref. [50] and the possibility of formation of Josephson loops in superconductor/ferromagnet/superconductor trilayers has been discussed in Ref. [51].

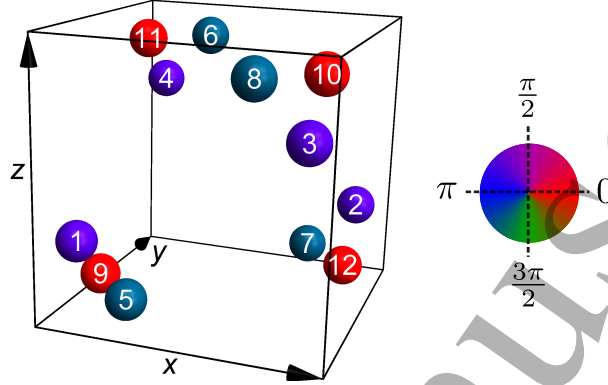


FIG. 3. Structure of the superconducting order parameter at the simplest TRS-breaking instability described in the main text for the  $\text{Re}_6(\text{Zr}, \text{Hf}, \text{Ti})$  superconductor family. Each sphere represents one of the 12 symmetrically distinct Re sites within the unit cell. The phase of the order parameter is shown in the color wheel.

### III. POSSIBLE REALIZATION OF THE LOOP SUPERCURRENT STATE: $\text{Re}_6\text{X}$ ( $\text{X} = \text{Zr}, \text{Hf}, \text{Ti}$ )

The ideas developed in the previous sections can be applied to the recently discovered  $\text{Re}_6\text{X}$  ( $\text{X} = \text{Zr}, \text{Hf}, \text{Ti}$ ) [12–14, 30–33] family of superconductors which break TRS at  $T_c$  but are otherwise fully conventional. We show here that this apparent contradiction can be explained by the spontaneous formation of a loop supercurrent state. These superconductors have a noncentrosymmetric body-centered cubic crystal structure (space group  $\text{I}\bar{4}3\text{m}$ – symmorphic with corresponding point group  $T_d$ ). A unit cell contains approximately 8 formula units (48 Re atoms and 10 X atoms). The Re atoms are distributed in two symmetrically equivalent groups each containing 24 atoms whereas the other atoms form two symmetrically distinct groups containing 2 and 8 atoms respectively. Within the group of 24 Re atoms, there are two symmetrically distinct groups each containing 12 atoms. The possible superconducting instabilities in the system can be understood by considering the symmetry properties of one of these groups having the fewest number of symmetries.

Following the procedure outlined above, the IPS is a real symmetric matrix of order 12 parameterized by 6 real parameters  $q_i$  with  $i = 1, \dots, 6$  (see Appendix B). Depending on the values of these parameters, there arise several degenerate eigenvalues and as a result the quartic order term in the Ginzburg-Landau free energy can stabilize a loop supercurrent state. We illustrate this by considering specific parameter values:  $\{q_i\} = \{1/3, 1/5, 1/7, 1/9, 1/11, 1/15\}$  as an example. The simplest instability with finite loop supercurrents for this case corresponds to a two-fold degenerate eigenvalue of the IPS matrix. Proceeding in the same way as before, the fourth-order term of the Ginzburg-Landau free energy can be shown to spontaneously stabilize the exotic loop supercurrent state with broken TRS below  $T_c$  (see Appendix B). The structure of the corresponding order parameter is shown in the Fig. 3. It is to be noted that our analysis merely shows the compatibility of the loop supercurrent instability with the crystal structure of the  $\text{Re}_6\text{X}$  materials and to compare with experiments we need microscopic computation of the spectrum which is beyond the scope of the present work.

In contrast to the above results, a similar analysis for  $\text{La}_7(\text{Ir}, \text{Rh})_3$  shows that no loop supercurrent instabilities are allowed for the crystal structure because the quartic part of the free energy does not stabilise a degenerate state with non-trivial complex phases. The superconducting ground state with broken TRS in these systems must therefore involve inter-site, inhomogeneous or triplet pairing.

#### IV. SPONTANEOUS MAGNETIC FIELDS

A magnetic moment is expected to spontaneously develop in the loop supercurrent ground state. We can estimate a rough upper bound using the Josephson formula [52]  $I_S \approx I_c \sin(\Delta\Phi_{i,j})$  to calculate the current along the bonds in our toy model marked with arrows in Fig. 1 (e) and (f). Here  $I_S$  is the Josephson current along a bond,  $I_c$  is the critical current of that bond and  $\Delta\Phi_{i,j} = \Phi_i - \Phi_j$  is the phase difference between the pairing potentials  $\Delta_i = |\Delta_i|e^{i\Phi_i}$  at sites  $i$  and  $j$ . An upper bound is thus  $I_S \lesssim I_c$ . The critical current can be estimated using the Ambegaokar-Baratoff formula [53]

$$I_c \approx \frac{\pi|\Delta(0)|}{2e} G_N \quad (7)$$

for a weak link of conductance  $G_N$  between two identical BCS superconductors with the zero-temperature gap  $\Delta(0)$ . Using the Landauer formula [54]:  $G_N = G_0 T$  for the conductance, where  $G_0$  is the conductance quantum and  $T$  is the transmission coefficient of the link, and taking  $T = 1$  as an absolute upper bound, we obtain

$$\frac{\mu^{max}}{\mu_B} \lesssim \Delta(0)m_e a^2 / \hbar^2 \quad (8)$$

where  $m_e$  is the mass of an electron and  $\mu_B$  is the Bohr magneton. This corresponds to an upper bound for the induced internal magnetic fields  $B_{int}^{max} \sim \mu_0 \mu^{max} / a^3$  ( $\mu_0$  is the vacuum permeability). Substituting the typical parameter values for the  $\text{Re}_6\text{X}$  family,  $a \sim 5\text{\AA}$  and  $\Delta(0) \sim 2k_B T_c$  with  $T_c \sim 5\text{K}$  we obtain  $B_{int}^{max} \sim 1$  Gauss which is consistent with the zero-field  $\mu\text{SR}$  experiments on these materials [12–14, 30].

#### V. CONCLUSIONS

We have shown using a toy model that in crystal lattices with a sufficiently large number of distinct, but symmetry-related sites within the unit cell the superconducting ground state can break TRS even for translational-invariant, onsite, intra-orbital and singlet pairing. This involves the formation of microscopic supercurrent loops within a unit cell. Several such materials surprisingly have many features which are usually associated with conventional, BCS superconductors and our proposal suggests a natural way to solve this puzzle. We have shown that the crystal structure of the  $\text{Re}_6(\text{Zr}, \text{Hf}, \text{Ti})$  family, representative of such systems, satisfies the requirements of this exotic superconducting instability. We have estimated an upper bound for the resulting spontaneous internal fields which is of similar order to that seen in  $\mu\text{SR}$  experiments on these systems. In addition to its possible relevance to actual materials, one might speculate that superconducting-dielectric meta-materials made of conventional superconductors [55, 56] could be engineered to realize this state.

To establish whether inequalities such as Eq. (4), which determine whether the loop supercurrent instability or a more conventional BCS-type instability dominates the phase diagram, are obeyed in a particular microscopic model is outside the scope of the symmetry-based arguments presented here. It is nevertheless interesting to speculate what would be the key ingredients of such a model. In a mean field theory, the GL parameters in Eq. (4) would be given by a sum of products of normal state Green's functions [36] and are functions of hybridizations between the different bands in the system. Different situations can occur depending on the distance between sites, hybridisation between orbitals, and any spatial structure of the effective interaction. All of these factors need to be taken into account in an actual microscopic calculation. However, the important point to note here is that there is no fundamental distinction between the GL parameters  $p_2$  and  $p_3$ , and therefore there is no reason why in general one or the other could be expected to be generically larger.

Our discussion has focused on the bulk properties of possible loop supercurrent superconductors. Our theory should also lead to domain formation and non-trivial order parameter reconstructions at domain boundaries, interfaces and around crystal defects. The magnetic moment textures that may result will, however, need to be described in order to predict the  $\mu\text{SR}$  experiments quantitatively. The nature of the collective excitations of such state and the energetics driving its competition with other, more conventional superconducting phases in specific materials remain to be explored.

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### Appendix A: Explicit form of the Ginzburg-Landau free energy for the toy model

We consider that the two-fold degenerate eigenvalue of the IPS matrix in Eq. 3 of the toy model first becomes negative below  $T_c$ , i. e. Eq. 4 is satisfied. The Ginzburg-Landau free energy in Eq. 6 corresponding to this doubly degenerate instability can now be evaluated. The second order term is

$$\mathcal{F}_2 = (|\eta_L|^2 + |\eta_R|^2)(T - T_c)\hat{\alpha} \quad (\text{A1})$$

where,  $(T - T_c)\hat{\alpha} \equiv \lambda$  with  $\lambda = (p_1 - p_2)$  being the degenerate eigenvalue of the  $\hat{\alpha}$  matrix and we assume  $\hat{\alpha} > 0$ . The fourth order term is given by

$$\begin{aligned} \mathcal{F}_4 = & \beta'_1 |\eta_L|^4 + \beta'_2 |\eta_R|^4 + (\beta'_3 \eta_L^{*2} \eta_R^2 + \beta'_3 \eta_L^2 \eta_R^{*2}) + 2|\eta_L|^2 (\beta'_4 \eta_L^* \eta_R + \beta'_4 \eta_L \eta_R^*) \\ & + 2|\eta_R|^2 (\beta'_5 \eta_L \eta_R^* + \beta'_5 \eta_L^* \eta_R) + 4|\eta_L|^2 |\eta_R|^2 \beta'_6 \end{aligned} \quad (\text{A2})$$

where,  $\beta'_1 = \langle L | \langle L | \hat{\beta} | L \rangle | L \rangle$ ,  $\beta'_2 = \langle R | \langle R | \hat{\beta} | R \rangle | R \rangle$ ,  $\beta'_3 = \langle L | \langle L | \hat{\beta} | R \rangle | R \rangle$ ,  $\beta'_4 = \langle L | \langle L | \hat{\beta} | L \rangle | R \rangle$ ,  $\beta'_5 = \langle R | \langle R | \hat{\beta} | L \rangle | R \rangle$  and  $\beta'_6 = \langle L | \langle R | \hat{\beta} | L \rangle | R \rangle$  are the only nonzero elements of the fourth order tensor  $\hat{\beta}$  using its general symmetry properties [57]. Requiring  $\mathcal{F}_4$  to be real, all the elements of the  $\hat{\beta}$  tensor are also real. Then we have

$$\begin{aligned} \mathcal{F}_4 = & \beta'_1 |\eta_L|^4 + \beta'_2 |\eta_R|^4 + \beta'_3 (\eta_L^{*2} \eta_R^2 + \eta_L^2 \eta_R^{*2}) + 2|\eta_L|^2 \beta'_4 (\eta_L^* \eta_R + \eta_L \eta_R^*) \\ & + 2|\eta_R|^2 \beta'_5 (\eta_L \eta_R^* + \eta_L^* \eta_R) + 4|\eta_L|^2 |\eta_R|^2 \beta'_6 \end{aligned} \quad (\text{A3})$$

The total free energy  $\mathcal{F} = \mathcal{F}_2 + \mathcal{F}_4$  is invariant under TRS. This condition together with the onsite singlet pairing interaction under consideration, for the model system, imply that  $\mathcal{F}(\eta_L, \eta_R) = \mathcal{F}(\eta_R^*, \eta_L^*)$ . Then we have  $\beta'_1 = \beta'_2$  and  $\beta'_4 = \beta'_5$ . Redefining the parameters as  $\beta'_1 = \beta_1$ ,  $\beta'_3 = \beta_2$ ,  $\beta'_4 = \beta_3$  and  $(2\beta'_6 - \beta'_1) = \beta_4$ ; we can rewrite

$$\mathcal{F}_4 = \beta_1 |\eta|^4 + \beta_2 (\eta_L^{*2} \eta_R^2 + \eta_L^2 \eta_R^{*2}) + 2\beta_3 |\eta|^2 (\eta_L^* \eta_R + \eta_L \eta_R^*) + 2\beta_4 |\eta_L|^2 |\eta_R|^2. \quad (\text{A4})$$

We use the parametrization  $|\eta_L| \equiv |\eta| \cos(\gamma)$  and  $|\eta_R| \equiv |\eta| \sin(\gamma)$  where  $0 \leq \gamma \leq \pi/2$ , and define  $\theta \equiv (\varphi_L - \varphi_R)$  where  $0 \leq \theta \leq 2\pi$ . The free energy can now be written in the canonical form shown in Eq. 6 with the effective Ginzburg-Landau  $b$ -parameter given by

$$b_{eff}(\theta, \gamma) = \left[ \beta_1 + \frac{1}{2} \sin^2(2\gamma) \{ \beta_4 + \beta_2 \cos(2\theta) \} + 2\beta_3 \sin(2\gamma) \cos(\theta) \right].$$

We note that the free energy has the following properties:  $\mathcal{F}(\theta, \gamma) = \mathcal{F}(2\pi - \theta, \gamma)$ , and  $\mathcal{F}(\theta, \gamma) = \mathcal{F}(\theta, \pi/2 - \gamma)$  - a result of invariance under TRS. Assuming  $a_{eff} < 0$  for  $T < T_c$ , the free energy is stable for  $b_{eff} > 0$ . The system then spontaneously chooses the nonzero order parameter value  $|\eta| = \eta_0$  given by

$$\left. \frac{\partial \mathcal{F}}{\partial |\eta|} \right|_{|\eta|=\eta_0} = 0, \quad (\text{A5})$$

where  $\eta_0 = \sqrt{-\frac{a_{eff}}{2b_{eff}}}$ . The value of the extremized free energy is

$$\mathcal{F}_0(\theta, \gamma) = -\frac{a_{eff}^2}{4b_{eff}}. \quad (\text{A6})$$

So, the free energy is minimum at points where  $b_{eff}$  is minimum. Its behavior for a particular set of  $\beta_i$  parameters is shown in Fig. 2. The system spontaneously chooses a minimum with finite loop supercurrent thus breaking TRS spontaneously. From the corresponding values of  $\eta_L$  and  $\eta_R$  at the free energy minimum then the circulating loop supercurrent is computed using Eq. 1. The order parameter in the loop supercurrent ground state for the toy model, in general, takes the form:  $|\Delta\rangle = \Delta^{(0)} \{ |\Delta'_1| e^{i\varphi'_1}, |\Delta'_1| e^{i(\varphi'_1 + \pi)}, |\Delta'_2| e^{i\varphi'_2}, |\Delta'_2| e^{i(\varphi'_2 + \pi)} \}$  where  $\Delta^{(0)}$  is an overall complex factor,  $|\Delta'_j|$  is the pairing amplitude and  $\varphi'_j$  is the phase ( $j = 1, 2$ ). In general,  $|\Delta'_1| \neq |\Delta'_2|$  and  $\varphi'_1 \neq \varphi'_2$ , implying  $C_4$  symmetry is broken as well in this case.

## Appendix B: IPS matrix for the $\text{Re}_6\text{X}$ materials

To understand the possible superconducting instabilities in the  $\text{Re}_6\text{X}$  ( $\text{X} = \text{Zr}, \text{Hf}, \text{Ti}$ ) family of superconductors, we may consider only the symmetry properties of the group of 12 symmetrically distinct Re atoms which have the lowest symmetry. In this case, the IPS matrix  $\hat{\alpha}$  is a  $12 \times 12$  real, symmetric matrix parametrized by 6 real parameters  $q_i$  ( $i = 1, \dots, 6$ ). It takes the form

$$\hat{\alpha} = \begin{pmatrix} q_1 & q_2 & q_3 & q_3 & q_4 & q_5 & q_5 & q_6 & q_4 & q_5 & q_6 & q_5 \\ q_2 & q_1 & q_3 & q_3 & q_5 & q_6 & q_4 & q_5 & q_5 & q_6 & q_5 & q_4 \\ q_3 & q_3 & q_1 & q_2 & q_6 & q_5 & q_5 & q_4 & q_5 & q_4 & q_5 & q_6 \\ q_3 & q_3 & q_2 & q_1 & q_5 & q_4 & q_6 & q_5 & q_6 & q_5 & q_4 & q_5 \\ q_4 & q_5 & q_6 & q_5 & q_1 & q_2 & q_3 & q_3 & q_4 & q_5 & q_5 & q_6 \\ q_5 & q_6 & q_5 & q_4 & q_2 & q_1 & q_3 & q_3 & q_5 & q_6 & q_4 & q_5 \\ q_5 & q_4 & q_5 & q_6 & q_3 & q_3 & q_1 & q_2 & q_6 & q_5 & q_5 & q_4 \\ q_6 & q_5 & q_4 & q_5 & q_3 & q_3 & q_2 & q_1 & q_5 & q_4 & q_6 & q_5 \\ q_4 & q_5 & q_5 & q_6 & q_4 & q_5 & q_6 & q_5 & q_1 & q_2 & q_3 & q_3 \\ q_5 & q_6 & q_4 & q_5 & q_5 & q_6 & q_5 & q_4 & q_2 & q_1 & q_3 & q_3 \\ q_6 & q_5 & q_5 & q_4 & q_5 & q_4 & q_5 & q_6 & q_3 & q_3 & q_1 & q_2 \\ q_5 & q_4 & q_6 & q_5 & q_6 & q_5 & q_4 & q_5 & q_3 & q_3 & q_2 & q_1 \end{pmatrix}. \quad (\text{B1})$$

We illustrate the possibility of stabilizing the exotic loop supercurrent state in this system by taking the parameter values  $\{q_i\} = \{1/3, 1/5, 1/7, 1/9, 1/11, 1/15\}$  as an example. Then the eigenvalues of  $\hat{\alpha}$  are

$$\{\lambda_i\} = \{(0.102137, 0.102137, 0.102137), (0.137374, 0.137374, 0.137374), (0.274774, 0.274774, 0.274774), (0.459452, 0.459452), 1.53824\}. \quad (\text{B2})$$

We note that there are several degenerate eigenvalues including triply degenerate ones. This is simply because of the presence of higher-dimensional irreducible representations in the crystal point group. The simplest instability which has finite loop supercurrents in this case is associated with the doubly degenerate eigenvalue 0.459452. The two corresponding eigenvectors form an orthonormal basis in this doubly degenerate subspace. They are given by

$$|\chi'_1\rangle = \frac{1}{2\sqrt{6}}(-1, -1, -1, -1, -1, -1, -1, -1, 2, 2, 2, 2) \equiv \frac{1}{2\sqrt{6}}|1\rangle; \quad (\text{B3})$$

$$|\chi'_2\rangle = \frac{1}{2\sqrt{2}}(1, 1, 1, 1, -1, -1, -1, -1, 0, 0, 0, 0) \equiv \frac{1}{2\sqrt{2}}|2\rangle. \quad (\text{B4})$$

Note that it is also possible to construct the following alternative basis set:

$$|L\rangle = \frac{|\chi'_1\rangle + i|\chi'_2\rangle}{\sqrt{2}}; \quad |R\rangle = \frac{|\chi'_1\rangle - i|\chi'_2\rangle}{\sqrt{2}}. \quad (\text{B5})$$

The vectors  $|L\rangle$  and  $|R\rangle$  are related by TRS and are thus analogous to the counter-circulating states displayed in the Figs. 1(e) and (f) for the toy model. Here we work instead with real eigenvectors for convenience. The order parameter in this degenerate subspace is written as

$$|\Delta\rangle = \eta_1|1\rangle + \eta_2|2\rangle. \quad (\text{B6})$$

The quartic order term in the Ginzburg-Landau free energy, constructed in the same way as in the Appendix A, is given by

$$\mathcal{F}_4 = \beta_1(|\eta_1|^4 + 9|\eta_2|^4) + (3\beta_1 - 2\beta_2)[(\eta_1^*\eta_2)^2 + (\eta_1\eta_2^*)^2] + 4\beta_2|\eta_1|^2|\eta_2|^2. \quad (\text{B7})$$

It is parametrized by the two Ginzburg-Landau parameters  $\beta_1$  and  $\beta_2$ . Minimizing the free energy we find that there two possible stable ground states. The first one corresponds to  $(\eta_1, \eta_2) = (1, 0)$  which is a conventional BCS type instability. The second one is for  $(\eta_1, \eta_2) = \frac{1}{\sqrt{2}}(1, i)$  which is a TRS breaking instability stabilized in the parameter regime  $-\frac{1}{2} < \frac{\beta_2}{\beta_1} < \frac{3}{4}$ . The ground state order parameter, for this instability, is then given by

$$\begin{aligned} |\Delta\rangle &= \frac{1}{\sqrt{2}}(|1\rangle + i|2\rangle), \\ &= \{\Delta_1, \Delta_1, \Delta_1, \Delta_1, \Delta_2, \Delta_2, \Delta_2, \Delta_2, \Delta_3, \Delta_3, \Delta_3, \Delta_3\} \end{aligned} \quad (\text{B8})$$

where  $\Delta_1 = e^{i3\pi/4}$ ,  $\Delta_2 = e^{i5\pi/4}$  and  $\Delta_3 = \sqrt{2}$ . Clearly, if the TRS breaking instability is realized in the two-fold degenerate channel, the superconducting ground state for the  $\text{Re}_6\text{X}$  materials will have finite loop supercurrents. Evidently the ground state above in Eq. (B8) is proportional to  $|L\rangle$  in Eq. (B5) which is degenerate with its time-reversed partner  $|R\rangle$ , in complete analogy with our toy model.

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10  $\otimes | m_4 \rangle) = (\langle m_2 | \otimes \langle m_1 |) \hat{\beta} (| m_4 \rangle \otimes | m_3 \rangle)$  where  $m_i = L$  and  $R$  ( $i = 1, \dots, 4$ ).  
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